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## CONTAINER STOPPER

#### **Technical Field**

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The present invention relates to an improved container stopper for stoppering an opening in a container, and a packaged product incorporating such an improved stopper. The invention also relates to an improved method of forming container stoppers

A number of products are packaged in containers where the opening in the container is sealed using a stopper. In these circumstances, the stopper typically forms an interference fit within the container opening. One of the most common examples of a packaged product that uses such a stopper is wine, although other beverages and edible oils are also common examples. The improved container stopper of the present invention has particular application as a cork-type stopper typically associated with bottles of wine and oil, although it will be appreciated that the invention is not limited to this particular type of container stopper, but may have application in other fields.

## **Background**

Wine is traditionally packaged in bottles that are sealed with cork stoppers. Stoppers made form cork have historically been used in the wine industry for a variety of reasons, most of which relate to the natural qualities of the cork that make it suitable for this purpose. By way of example, cork as a material is durable, resilient, free from rotting, is permeable to gas, is predominantly waterproof, is readily compressible and is easy to shape into a variety of desired conformations.

A disadvantage of using cork stoppers, however, is that they can lead to the development of undesirable scent and flavour characteristics in the packaged product. In particular, cork is known to be a cause of musty or mouldy taint in wine, and sometimes a cause of 'off' flavours due to oxidation. Indeed, it is estimated that approximately five percent of wines are affected in this way. In 1994 the Quercus project was initiated by the European cork industry to reduce the occurrence of poor or 'off' flavours. TCA (2,4,6 Trichloroanisole) has been

identified as the cause of some musty/mouldy taint. Although cork is not the only source of TCA in wine, it has been shown that some corks contain levels of TCA that are transferred to wine when stored in bottles. It has also been observed that the taints can be transferred to the wine via vapour when the bottles are left standing up and the liquid does not contact the cork surface. This is due to cork's poor barrier to volatile materials, demonstrated by its readiness to absorb and desorb moisture vapour with changes in relative humidity, its susceptibility to the entry of the volatiles which may be retained and later transferred to wine.

Another consideration is whether the product needs to be completely sealed off from the environment or whether gaseous exchange is desirable to improve the characteristics of the product. With bottle storage of wine, for example, flavour development of the wine with aging has to be taken into account. Although the concept of bottle aging, bottle maturation or bottle development is well known, it is in fact little understood or scientifically proven. There is some belief that the stopper breathes and that oxygen plays a role in bottle development of the wine, although it is well proven that too much oxygen will oxidise a wine and ruin it. There is a growing body of work that is developing the use of micro-oxygenation to develop flavour and mature wines. Any stopper for use in the wine industry therefore should be permeable to some extent to allow some oxygen to permeate the stopper and come into contact with the wine.

A number of approaches have been developed aimed at overcoming the problems of contamination of the product by the stopper whilst at the same time retaining the oxygen permeability characteristic. For example, it has been shown that coatings can be used to improve the performance of cork stoppers. Waxes and paraffins may be used as coating and applied to corks to improve the sealing capability. If this is done, paraffins are usually used in solid, oil or emulsion form. It has also been observed that wax coatings can reduce the amount of liquid that soaks into the cork over time. Silicone coatings have also been applied to corks to improve the insertion and extraction of the cork. It is thought that the silicone reduces the friction between the cork and the bottle during both the insertion and extraction processes. Coatings of this type are typically applied to the corks while

the corks are tumbling in a rotating drum. The corks may be tumbled with a solid wax block or a liquid is squirted or otherwise sprayed onto corks. The coating is then spread from cork to cork by the physical contact between the corks transferring the coating and evenly distributing it. Heat may also be applied to aid the process.

There have been attempts to place other types of physical barriers between the stopper and the wine to prevent the transmission of tainting components to the wine. Several of these attempts have worked on the principle of applying a coating layer in the form of a polymeric film to the end of the stopper. However, the characteristics of the stoppers produced using prior techniques have not always been satisfactory. Without wishing to be bound by theory it is thought that the problem with these approaches is that whilst the stopper is compressible (as required for insertion into the neck of the bottle) the coating layer is typically not compressible. This leads to the development of imperfections in the coating layer such as cracking, peeling, creasing and the like.

Patent application WO 00/34140 purports to overcome these problems and describes a composite stopper with a body and a thick moulded elastomer plug at the end of the stopper in contact with the wine. The elastomer plug acts to seal the bottle and is claimed to be a taint barrier. While this approach may overcome the problems of taint, it does have its drawbacks. For example, the unit cost of each stopper is significantly higher than the unit cost of cork stoppers in general, and so is undesirable from an economic standpoint. In addition, elastomer plugs of the type described have a high inherent transmission rate for oxygen and tainting molecules such as TCA, thereby requiring the plug to be thick to achieve the required oxygen and taint barrier properties for desirable bottle aging and taint reduction. Further, as the exact orientation of the stopper into the opening of the container is crucial for proper performance of this particular stopper, expensive capping machinery is typically required to ensure adequate performance of the stopper once fitted.

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The present inventor made a study of prior art stoppers and found that many of the deficiencies observed with prior art coating techniques were apparently caused by the radial compression of the stopper during its insertion into a container opening. It was found that if the compression of the coating film could be reduced or at least evened out to some degree then problems associated with the use of such coating films could be ameliorated. One method of achieving this is described in co-pending application PCT/AU02/00877, which employs tapering at the end of the stopper and/or the use of uniformly compressible materials.

The present invention provides alternative solutions to those disclosed in the co-pending application. In particular, the applicant has found that by ensuring that the end of the stopper is uneven, such as by shaping the axially facing surface of the end of the stopper and/or by providing a foam material on the end of the stopper, improved performance of the stopper can be obtained.

Thus, the present invention aims to provide a new and improved stopper configuration, and a packaged product incorporating such a stopper.

## Summary of the Invention

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The present invention contemplates stoppers formed in a variety of shapes and configurations. The stoppers are usually elongate and may have any of a variety of cross-sectional shapes, with the cross-sectional shape typically determined by the shape of the opening the stopper is intended to seal. Most usually, however, the stopper will have a generally cylindrically shaped body. Accordingly, the end of the stopper adapted for insertion into the container opening will usually have a generally circular cross-sectional configuration and may present a generally planar axially facing end surface. The axially facing end surface of the stopper may not be entirely planar, however. For example, a peripheral edge region at the end of the stopper may be tapered or chamfered, and/or the end may have a stepped configuration forming a shoulder region. The end could also conceivably have a curved or rounded surface. As a result of the studies carried out by the inventors it was found that the provision of an uneven

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axially facing surface on the end of the stopper, provided superior stopper performance.

In one aspect the present invention provides a container stopper including a body of compressible material having at least one end for insertion into an opening of a container, and a film coating on at least part of said end of the body of compressible material for providing a protective barrier between the compressible material and the contents of the container, wherein the end of the stopper body has an uneven shaped axially facing surface. There are a number of ways in which the end of the stopper may be modified so that it has an uneven shaped axially facing surface. For example the axially facing end surface may include protrusions, recesses or a combination of these.

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In one preferred embodiment of the invention the end includes at least one recess, preferably a plurality of recesses. The recesses may take any of a number of suitable forms and may be regular or irregular in shape although it is preferred that the recesses are regular in shape. Alternatively there may be a combination of regular and irregular recesses on the stopper end. The recess(es) are preferably selected from the group consisting of dimples, depressions, grooves, slots, channels and indentations.

The recesses may vary considerably in size and in circumstances in which there are a plurality of recesses each recess may be the same or different in size and shape to the other recesses. In a preferred embodiment each recess has a depth of from 0.01 to 10 mm, more preferably from 0.05 to 5 mm, most preferably from 0.1 to 3 mm. Each recess preferably has a width of from 0.01 to 10 mm, more preferably from 0.05 to 7 mm, most preferably from 0.1 to 5 mm. The recesses may be spaced uniformly over the surface of the stopper end or placed irregularly although it is preferred that they are substantially uniformly placed. In a preferred embodiment each recess is spaced at a distance of from 0.01 to 10 mm from the adjacent recess(es), more preferably from 0.05 to 7 mm. most preferably from 0.1 to 5 mm from the adjacent recess(es).

In one preferred embodiment the recesses are dimples. The dimples may be of a number of different shapes with preferred dimples being hemispherical,

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ellipsoid or in the shape of a segment of a sphere. In another preferred embodiment the recesses are grooves, slots or channels. Once again these may take any of a number of suitable shapes. Nevertheless it is preferred that the cross section of the groove, channel or slot is selected from the group consisting of semi-circular, triangular, square, rectangular, trapezoidal or wedged.

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In another preferred embodiment the recesses may be indentations. The indentations may take a number of forms however it is preferred that they are cubic, cuboid, truncated cuboid, tetrahedral, truncated tetrahedral, pyramidal, truncated pyramidal, frusto-pyramidal, cylindrical, truncated cylindrical, conical, truncated conical or frusto-conical in shape.

The recesses may be chosen such that all the recesses in the end of the stopper are of the same general type or a variety of different recesses may be used with the same stopper. Thus, for example a stopper may include both grooves and indentations. Alternatively, a stopper may include indentations and dimples. In general, however, it is preferred that the recesses in any given stopper are of the same general type. Each recess may differ in size from the other recesses used in the stopper end. Nevertheless for ease of manufacture it is preferred that each recess of the same general type is of the same general size.

In one preferred embodiment the recesses are concentric grooves, slots or channels. In this embodiment it is preferred that the concentric recesses are of a size and spacing to form a concentric corrugation on the stopper end.

In another preferred embodiment the recesses are selected from the group consisting of grooves, slots and channels and extend across at least a portion of the axially facing end surface of the stopper. In this embodiment it is particularly preferred that the recesses extend across the entirety of the axially facing end of the stopper. The recesses may all extend generally in the same direction or they may extend in a number of different directions. In one preferred embodiment the recesses form a set of recesses radiating from a common point of the end of the stopper, preferably radiating from the centre of the end of the stopper. Alternatively, the recesses may form a dendritic or a crosshatch pattern

on the end of the stopper. In a particularly preferred embodiment a first set of recesses extend in one direction and a second set of recesses extend in a second direction such that each of the recesses in the first set intersect with one or more of the recesses in the second set. The minor angle of incidence of the sets of recesses can vary from 1° (where the recesses are almost parallel) to 90° (where the recesses are substantially parallel). When this occurs it is most preferred that the recesses in the first set are substantially perpendicular to the recesses in the second set. The positioning of the recesses may form a number of patterns on the axially facing end of the stopper, for example the end may be corrugated, castellated, or present a sawtooth or staggered saw tooth (where there are gaps between the teeth) style configuration.

In another preferred embodiment of the invention the axially facing end surface of the stopper includes a number of different regions, each region including a plurality of recesses. In a preferred form of this embodiment the recesses in each region are different. In another preferred embodiment the end includes an outer region that extends radially inwardly from an outermost periphery of the stopper end, said outer region enclosing an inner region, the recesses in the outer region being different to the recesses in the inner region. In one preferred form of this embodiment the recesses in the outer region are grooves, slots or channels and the recesses in the inner region are indentations. In another preferred form of this embodiment the recesses in the outer region are grooves, slots or channels that extend radially inwardly from the outermost periphery of the stopper end and the recesses in the inner region are concentric grooves, slots or channels. In this embodiment it is preferred that the stopper is a substantially cylindrical stopper.

In another preferred embodiment of the invention the end includes at least one protrusion, preferably a plurality of protrusions. The protrusions may take any of a number of suitable forms and may be regular or irregular in shape although it is preferred that they are regular in shape. Alternatively there may be a combination of regular and irregular protrusions on the stopper end. The protrusions are preferably in the form of projections or ridges.

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The protrusions may vary considerably in size and in circumstances in which there are a plurality of protrusion, each protrusion may be the same or different in size and shape to the other protrusions. In a preferred embodiment each protrusion has a height of from 0.01 to 10 mm, more preferably from 0.05 to 5 mm, most preferably from 0.1 to 3 mm. Each protrusion preferably has a base width of from 0.01 to 10 mm, more preferably from 0.05 to 7 mm, most preferably from 0.1 to 5 mm. The protrusions may be spaced uniformly over the surface of the stopper end or placed irregularly although it is preferred that they are substantially uniformly placed. In a preferred embodiment each protrusion is spaced at a distance of from 0.01 to 10 mm from the adjacent protrusions more preferably from 0.05 to 7 mm. most preferably from 0.1 to 5 mm from the adjacent protrusions.

In one preferred embodiment the protrusions are projections. The projections may take a number of forms however it is preferred that they are cubic, cuboid, truncated cuboid, tetrahedral, truncated tetrahedral, pyramidal, truncated pyramidal, frusto-pyramidal, cylindrical, truncated cylindrical, conical, truncated conical or frusto-conical in shape.

The protrusions may be chosen such that all the protrusions in the end of the stopper are of the same general type or a variety of different protrusions may be used with the same stopper. Thus, for example a stopper may include both projections and ridges. In general, however, it is preferred that the protrusions in any given stopper are of the same general type. Each protrusion may also differ in size from the other protrusions used in the stopper end. Nevertheless for ease of manufacture it is preferred that each protrusion of the same general type is of the same general size.

In one preferred embodiment the protrusions are concentric ridges. In this embodiment it is preferred that the concentric ridges are of a size and spacing to form a concentric corrugation on the stopper end.

In another preferred embodiment the protrusions are ridges that extend across at least a portion of the axially facing end surface of the stopper. In this embodiment it is particularly preferred that the ridges extend across the entirety

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of the axially facing end of the stopper. The ridges may all extend generally in the same direction or they may extend in a number of different directions. In one preferred embodiment the ridges form a set of ridges radiating from a common point on the end of the stopper, preferably from the centre of the end of the stopper. Alternatively, the ridges may form a dendritic or a crosshatch pattern on the end of the stopper. In a particularly preferred aspect of this embodiment a first set of ridges extend in one direction and a second set of ridges extend in a second direction such that each of the ridges in the first set intersect with one or more of the ridges in the second set. The minor angle of incidence of the sets of ridges can vary from 1° (where the ridges are almost parallel) to 90° (where the ridges are substantially parallel). When this occurs it is most preferred that the ridges in the first set are substantially perpendicular to the ridges in the second set. The positioning of the ridges may form a number of patterns on the axially facing end of the stopper. The ridges may thus form a crosshatch, sawtooth or staggered sawtooth pattern on the end of the stopper.

In another preferred embodiment of the invention the axially facing end surface of the stopper includes a number of different regions, each region including a plurality of protrusions. In a preferred form of this embodiment the protrusions in each region are different. In another preferred embodiment the end includes an outer region that extends radially inwardly from an outermost periphery of the stopper end, said outer region enclosing an inner region, the protrusions in the outer region being different to the protrusions in the inner region. In one preferred form of this embodiment the protrusions in the outer region are ridges and the protrusions in the inner region are projections. In another preferred form of this embodiment the ridges in the outer region are ridges that extend radially inwardly from the outermost periphery of the stopper end and the protrusions in the inner region are concentric ridges. In this embodiment it is preferred that the stopper is a substantially cylindrical stopper.

Whilst in the above embodiments there has been a detailed discussion with respect of stopper ends including protrusions or recesses a combination of these features may be present in the same stopper. As such in another preferred

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embodiment the end of the stopper includes both protrusions and recesses. In this embodiment the preferred form of the protrusions and recesses is as described previously. In this embodiment it is preferred that the end includes a plurality of different regions. A first region including protrusions and at least one further region including recesses.

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In the embodiments discussed above there is a film coating on at least a portion of the axially facing end of the stopper. In a preferred embodiment the film coating covers all the axially facing end surface of the end of the stopper.

In particularly preferred aspect the present invention provides a container stopper including a body of compressible material having at least one end for insertion into an opening of a container, and a film coating on at least part of said end of the body of compressible material for providing a protective barrier between the compressible material and the contents of the container, wherein the end of the stopper body includes a step or shoulder region at a periphery thereof and a substantially centrally-located protrusion.

It is preferred that the shoulder region of the stopper extends radially inwardly from an outermost periphery of the stopper end. The radial extent of the shoulder region is preferably substantially perpendicular to a longitudinal axis of the stopper. Thus, in the event that the stopper body is generally cylindrical, the step or shoulder region is a generally annular and encircles the central protrusion.

In a preferred embodiment the central protrusion has a generally cylindrical or frusto-conical form. Accordingly, the central protrusion preferably has a substantially planar endmost surface, and either cylindrical or conical side surfaces. Furthermore, this protrusion may optionally be partly recessed into the shoulder region such that a recess or groove in the shoulder region surrounds the base of the protrusion.

In a preferred embodiment, the film coating is provided on the outer surface of the centrally located protrusion. Preferably, the film coating substantially entirely covers the endmost surface of the centrally located protrusion only. Alternatively, the film coating may substantially entirely cover the

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outer surface of the centrally located protrusion, including the side surfaces thereof. The film coating may optionally also cover at least a portion of the step or shoulder region.

In another preferred embodiment the container stopper includes a region of foamed material provided at the end of the stopper body. The foamed material is preferably provided at the step or shoulder region, although it may also be provided on the centrally located protrusion. The foamed material is preferably a non-tainting and non-scalping material such as a foamed plastic.

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In a preferred embodiment of this aspect, the area of the step or shoulder region is more than 10% of the total surface area of the end of the stopper body, and more preferably more than 20% of the total surface area of the end of the stopper body (which includes the shoulder region).

In the invention it is preferred that the film coating is a polymeric film and preferably has multiple layers including at least one barrier layer and at least one adhesive layer. Any suitable barrier layer may be used. However, examples of preferred barrier layers include at least one polymer selected from the group consisting of: BOPP, polyacrylonitrile, polychlorotrifluoroethylene (PCTFE) polyethylene, polypropylene, polyethylene terephthalate (PET), polyvinyl chloride, polydivinyl chloride, polyvinylidene chloride (PVDC), polyvinyl dichloride, polyvinyl acetate, ethylene-vinyl alcohol (EVOH), polyvinyl alcohol (PVOH), nylons, polycarbonates, polystyrene, polyalkylene oxide polymers, and any possible copolymers of any of the foregoing. Preferred barrier layers may also be metallised. In addition it is preferred that the barrier layer include silica or aluminium oxide. Particularly preferred barrier layers include Nylon, PVDC, EVOH or are metallised.

The compressible material of the stopper is preferably selected from the group consisting of: natural cork, agglomerated cork and micro-agglomerated cork. Of course, a polymeric material such as a medium density or low density closed-cell foamed plastic (as disclosed in US patent 6,355,320) could also be used, as could a number of fibrous materials (as disclosed in US patent 5,665,462).

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One of the advantages of the present invention is that when the stopper sits compressed within the neck of a bottle, most of the compressive deformation is confined to the outer peripheral region of the stopper body. This leaves the film coating on the outer surface of the end of the stopper substantially unaffected by wrinkling, which in turn means that the protective barrier provided by the film suffers substantially reduced adverse affects.

According to another aspect, the present invention provides a container stopper including a body of compressible material having at least one end for insertion into an opening of a container, and a film coating on at least part of said end of the body of compressible material for providing a protective barrier between the compressible material and the contents of the container, wherein the end of the stopper body includes region of foamed material. This region of foamed material is also able to reduce the adverse effects of wrinkling.

Preferably, the foamed material includes a polymer selected from the group of polymers mentioned herein as being suitable or preferred for the barrier layer of the film coating on the end of the stopper body. The foamed material is preferably a closed-cell type foamed polymer.

In a preferred embodiment the end of the stopper body tapers towards an endmost surface of the stopper and the foamed material is provided in the region of taper. Preferably, a peripheral edge region at the end of the stopper is tapered or chamfered and the foamed material is located at the peripheral edge region. Indications are that for technical performance, the foam is only required at the peripheral edge region. For practical ease in production of the stopper, however, it is sometimes preferable for the foam to cover the entire end of the stopper.

In another preferred embodiment the end of the stopper body includes a step or shoulder region at a peripheral edge region thereof and the foamed material is provided in the shoulder region. The end of the stopper body also preferably includes a substantially centrally located protrusion.

The shoulder region of the stopper extends radially inwardly from the outer periphery of the stopper end, with the radial extent of the shoulder region preferably being substantially perpendicular to a longitudinal axis of the stopper.

Thus, in the event that the stopper body is generally cylindrical, the step or shoulder region is a generally annular and encircles the central protrusion. As already described, the central protrusion preferably has a generally cylindrical or frusto-conical form. Accordingly, the central protrusion preferably has a substantially planar endmost surface, and either cylindrical or conical side surfaces. Furthermore, this protrusion may optionally be partly recessed into the shoulder region such that a recess or groove in the shoulder region surrounds the base of the protrusion.

According to a further aspect, the present invention provides a packaged product including a liquid in a container, such as a bottle. The container includes a container stopper according to the invention as described with respect to either aspect above, with the container stopper received in an opening of the container (typically formed in a neck of the bottle) in an interference fit to thereby seal the container opening.

The stoppers of the invention can be used for the storage of a wide range of materials. It is preferred that the material is a fluid, particularly beverages including wine, edible oils, and even chemicals such as acids.

The present invention also provides methods of making the stoppers of the invention. Accordingly in a further aspect the invention provides a method of producing a container stopper the method including the steps of

- (a) providing a container stopper, said stopper having a body of compressible material having at least one end, said end presenting a surface;
- (b) providing a film,

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- (c) heating the film,
- 25 (d) pressing the film and the surface relatively together so as to attach the film to the surface,
  - (e) pressing the product of step (d) with a cooling plate, the cooling plate being shaped in such a manner to introduce protrusions or recesses onto the end of the stopper after cooling, wherein step (c) occurs either prior to or simultaneously with step (d).

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In this aspect of the invention it is preferred that the cooling plate includes a number of protrusions to produce a stopper including a number of recesses in the end. Alternatively the cooling plate may include a number of recesses to produce a stopper including a number of protrusions. In a preferred embodiment of the method the film is heated to a temperature greater than the softening, melting or activation temperature of the outer layer of the polymeric film. It is also preferred that the pressing during step (d) is sufficient to compress the stopper by at least 0.2% in the axial direction, more preferably by at least 5% in the axial direction. It is preferred that the pressing continues for a period of from 0.1 to 5 seconds.

## **Brief Description of the Drawings**

For assistance in arriving at a better understanding of the present invention, examples of a container stopper according to preferred embodiments of the invention are hereafter described with reference to the accompanying drawings. The preceding description may also be read with reference to those drawings. However, it should be understood that the drawings are not intended to limit the generality of the preceding description.

In the drawings, like reference numerals designate like features and:

- Fig. 1 shows a schematic side view of an end of a container stopper according to a preferred embodiment of the invention;
- Fig. 2 shows a schematic side view of an end of a container stopper according to another preferred embodiment of the invention;
- Fig. 3 shows a schematic side view of an end of a container stopper according to a further preferred embodiment of the invention;
  - Fig. 4 shows a schematic side view of an end of a container stopper according to yet another preferred embodiment of the invention;
- Fig. 5 shows a schematic side view of an end of a container stopper according to a further preferred embodiment of the invention;
- Fig. 6 shows a schematic side view of an end of a container stopper according to still another preferred embodiment of the invention;

Fig. 7 shows a schematic side view of an end of a container stopper according to yet a further preferred embodiment of the invention; and

- Fig. 8 shows a schematic side view of an end of a container stopper according to another preferred embodiment of the invention.
- Fig. 9 shows a schematic side view of an end of a container stopper according to a preferred embodiment of the invention;
- Fig. 10 shows a plan view of an end of a container stopper according to another preferred embodiment of the invention;
- Fig. 11 shows a plan view of an end of a container stopper according to a further preferred embodiment of the invention;
- Fig. 12 shows a schematic side view of an end of a container stopper according to yet another preferred embodiment of the invention;
- Fig. 13A, 13B and 13C show fragmentary side views of further preferred embodiments of the invention;
- Fig. 14 shows a plan view of an end of a container stopper according to another preferred embodiment of the invention;

# **Detailed Description of the Preferred Embodiments**

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In the wine industry, bottling operations typically utilise high speed stoppering machines which subject the cork-type stoppers to large compression forces. These machines typically have a number of compression jaws, which radially compress the stopper from its normal diameter to about half of its original size. The machines then employ a ram to force the compressed stoppers directly into the bottle openings where the stoppers expand creating a tight interference fit in the neck of the bottles, and thus seal the bottle.

Naturally, therefore, the stoppers of the present invention should have a compressible body. It is preferred that the stopper body be formed of a material that can be compressed by at least 5 percent, more preferably by at least 10 percent, even more preferably by at least 20 percent, and preferably by at least 30 percent. A number of materials having these properties may be used. Most preferably, however, the stoppers produced with the present invention have

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bodies formed from natural cork, agglomerated cork, micro-agglomerated cork, or a combination thereof. Alternatively, the stopper body may be made from a polymeric material. For example, the stopper body may comprise medium density or low density, closed cell foamed plastic. Such foam plastics may comprise one or more polymers selected from the group consisting of plastic polymers, inert polymers, homopolymers, copolymers, terpolymers, thermoplastic elastomers, and thermoplastic olefins. In such applications it is preferred that the closed cell foam plastic material comprises at least one polymer selected from the group consisting of polyethylenes, metallocene catalysed polyethylenes, polybutanes, polybutylenes, polyurethanes, silicones, vinyl based resins, polyesters, ethylenic acrylic copolymers, ethylene-vinyl-acetate copolymers, ethylene-methyl-acrylate copolymers. ethylene-butyl-acrylate copolymers. ethylene-propylene-rubber, styrene butadiene rubber, ethylene-ethyl-acrylic copolymers, ionomers, polypropylenes, copolymers or polyporpylenes and the like. Examples of these types of materials are provided in U.S. patent 6,355,320.

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As discussed above, the stopper body can also be made of fibres. Fibre closure bodies are discussed in U.S. 5,665,462 and include interalia vegetable fibres such as cotton, flax, sisal, linen, cellulose and jute, and animal-derived fibres such as angora, wool, alpaca, and mixtures thereof. Synthetic fibres can also be used including cellulose acetate, cellulose triacetate, acrylics, aromines (aromatic polyamines), rayons, polyolefins (e.g. polypropylene), nylonspolyesters, polyurethanes, terylenes, teflon and mixtures thereof. Of course, mixtures of the synthetic and/or natural fibres may also be used in certain embodiments.

The stoppers are usually elongate and may have any of a variety of cross-sectional shapes, with the shape of the stopper essentially being determined by the shape of the opening it is intended to seal. For example if the stopper is in the form of a champagne cork it typically will have a diameter of approximately 30 mm. As mentioned previously, however, the stoppers will most typically have a generally cylindrical body, with the standard dimensions being 24mm diameter and 45mm length.

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The stoppers also have a film applied to at least a part of the end stopper inserted into the bottle-neck opening. The film may cover only a portion of the end of the stopper or cover the entirety of the end of the stopper. It is preferred that the film covers all the axially facing end surface of the stopper. The film is preferably a polymeric film, and it typically has multiple layers, including an outer barrier layer and an inner adhesive layer.

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The barrier layer preferably has a low permeability to hydrogen, oxygen and carbon dioxide, and is substantially impermeable to organic molecules with molecular weights greater than 40. A number of barrier layers are known in the art that can be utilised to achieve this result. Preferably, the barrier layer includes one or more polymers selected from the group consisting of BOPP, polyacrylonitrile and copolymers thereof, polychlorotrifluoroethylene (PCTFE), polyethylene and copolymers thereof, polypropylene and copolymers thereof, polyethylene Terepthalate (PET) and copolymers thereof, ethylene-vinyl acetate and polyvinyl acetate and copolymers thereof, polyvinylchloride and copolymers polyvinylidenechloride thereof. (PVDC) and copolymers thereof, polydivinylchloride and copolymers thereof, polyvinyldichloride and copolymers thereof, polyvinylacetate and copolymers thereof, ethylene vinyl alcohol (EVOH) and copolymers thereof, polyvinyl alcohol (PVOH) and copolymers thereof, nylon, ethylene acrylic acetate, ethylene acetic alcohol, polyurethane and copolymers thereof, cellophane, polyamines, polycarbonates, polystyrene and copolymers thereof, polyalkylene oxides and copolymers thereof, polyethylene oxides and copolymers thereof, cellulose, cellulose derivatives, and metal, aluminium oxide, silica and silicon polymers. A preferred barrier film has a multi-layer structure and includes PVDC, PDVC, EVOH, nylon, EAA or metal. In addition it is preferred that the barrier layer include silica or aluminium oxide.

The barrier layer preferably has a thickness in the range of 1 to 50 micron, more preferably in the range of 2 to 20 micron, even more preferably and most preferably in the range of 5 to 15 micron.

The adhesive layer may be laminated to the barrier layer, or it may be added to the film or cork by way of a spray or extrusion. Suitable adhesive layers

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include heat activated adhesive compounds (eg in a laminated layer) and hotmelt adhesive compounds (eg applied to the film as a spray). Suitable adhesive compounds therefore include ethylene vinyl acetate, polyamides, acrylics, methyl methacrylate based polymers, starch based adhesive, carbohydrate based adhesives, protein based adhesives, animal glues, rubber, silicone, epoxy, melamine-formaldehyde based, unsaturated polyesters, urea-formaldehyde resins. resorcinol, phenolic, anaerobic adhesives, urethanes. EAA, polyurethanes, polyethylene, polysulfides, polyvinyl and ethylene vinyl acetates. Particularly preferred adhesives are ethylene vinyl acetate homo-polymer or copolymer.

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The adhesive layer preferably has a thickness in the range of 0.1 to 40 micron, more preferably 0.1 to 10 micron, and more preferably in the range of 1 to 5 micron. If a heat-activated adhesive is used, it preferably has an activation temperature greater than about 40°C, more preferably greater than about 60°C, and most preferably greater than about 80°C.

Referring to all of Figs. 1 to 8, 9, 12 and 13 of the drawings, various examples of an end (1) of a cork-type stopper are shown in side view. The corks have a generally cylindrical body having a diameter ( $\phi$ ) equal to about 24 mm. The overall length of the cork body is typically about 45 mm. The end (1) of the stoppers shown in the drawings are adapted for insertion into the neck opening of a wine bottle, and include a coating of polymeric film (F) to provide a protective barrier between the cork material and the contents of the bottle.

Referring now to Fig. 1 of the drawings, an end (1) of a particular cork-type stopper is shown in side view. This end (1) of the cork body includes on its axially facing surface a step or shoulder region (2) at the periphery, which forms a centrally located protrusion (3). The step or shoulder region (2) of the stopper extends radially inwardly from an outermost periphery of the cylindrical body substantially perpendicularly to a longitudinal axis of the cork. The width (x) of the shoulder region (2) is typically in the range of about 0.5 mm to about 3 mm, and more preferably in the range of about 1 mm to about 2 mm. Accordingly, the shoulder region (2) is typically in the form of an annular flat surrounding the

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substantially centrally located protrusion (3). These dimensions for the shoulder region (2) are also generally applicable to the examples shown in Figs. 2 to 6.

As is clear from Figs. 1 and 2 of the drawings, the protrusion (3) has the general form of a squat cylinder, with a substantially planar endmost surface (4) and cylindrical side surfaces (5). The height (h) of the protrusion beyond the annular flat of the shoulder region (2) is typically in the range from about 1 mm to about 5 mm, and preferably in the range from about 2 mm to about 4 mm. These dimensions for the protrusion (3) are also generally applicable to the examples shown in Figs. 3 to 6. The film coating (F) covers substantially the entire outer surface of the protrusion, including the endmost surface (4) and the side surfaces (5). An annular region of foamed material (6) is also provided around the peripheral shoulder region (2).

Fig. 2 of the drawings shows a side view of the end (1) of a cork-type stopper having a configuration substantially the same as that shown in Fig. 1. The main difference is that the region of foamed material (6) extends as a layer over substantially the entire axially facing surface of the end including outer surfaces (4,5) of the protrusion, as well as over the shoulder region (2).

Figs. 3 and 4 of the drawings illustrate further examples of cork-type stoppers according to the present invention. In each of these cases, the protrusion (3) has a substantially frusto-conical form extending from the flat annular step or shoulder region (2) at the peripheral edge of the stopper body. Accordingly, the endmost surface (4) of the protrusion is still substantially planar, but the side surfaces (5) of the protrusion now have a conical taper. The film coating (F) is again applied to substantially cover the entire outer surface, i.e. both the endmost and side surfaces (4,5) of the protrusion. In Fig. 4, the annular shoulder region (2) also again includes a layer of foamed material (6) similar to the example shown in Fig. 2.

Referring now to Figs. 5 and 6 of the drawings, side views of the insertion end (1) of two further cork-type stoppers are illustrated. In these examples, the protrusion (3) is again of frusto-conical form, as in Figs. 3 and 4. In these examples, however, the protrusion (3) is partly recessed into the step or shoulder

region (2) such that a circular recess or groove (7) surrounding the base of the protrusion (3) is formed in the shoulder region. This recess or groove (7) is substantially circular and typically has a depth in the range from about 0.25 mm to about 1.5 mm, and more preferably in the range from about 0.5 mm to 1 mm. The polymeric film (F) applied to the end of the cork body again covers substantially the entire outer surface of the protrusion including both the substantially planar endmost surface (4) and the conical side surfaces (5). The example in Fig. 6 of the drawings is similar to that in Fig. 5, but includes a region of foamed material (6) provided in the step or shoulder region (2) at the base of the protrusion (3). The foamed material (6) does not cover the entire shoulder region but may optionally fill the recess or groove (7).

Figs. 7 and 8 illustrate examples in which the end (1) of the cork body has a peripheral edge region, which is chamfered or tapers to a substantially planar endmost surface (4). The endmost surfaces and the tapered/chamfered peripheral edge region are both coated with the polymeric film (F). In Fig 7, the endmost and chamfered surfaces are also covered with a layer of the foamed material (6). In Fig. 8, just the tapered region includes the layer of foamed material (6).

In figure 9 there is illustrated an embodiment wherein the end (1) has a film (F) which covers the axially facing surface of the end of the cork. The axially facing end surface includes a number of recesses in the form of grooves in the end with the groove width (v) and groove depth (y) being depicted. In general the recess will be such that the depth (y) is in the range of from 0.01 to 10 mm, more preferably from 0.05 to 5 mm, most preferably from 0.1 to 3 mm. The groove width (v) can also vary with the preferred width being in the range of 0.1 to 10 mm, more preferably 0.05 to 7mm, most preferably 0.1 to 5 mm. Whilst the diagram depicts a situation in which the grooves are contiguous forming a corrugated surface this is not required and there could be relatively planar portions of the end separating adjacent grooves. If this occurs it is preferred that the distance between adjacent grooves is in the range of 0.1 to 10 mm, more preferably 0.05 to 7mm, most preferably 0.1 to 5 mm.

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In figure 10 there is depicted plan view of a further preferred embodiment. In this embodiment there are a number of concentric grooves (R) that are located in the axially facing surface of the end of the cork.

In figure 11 there is a depiction of a plan view of an end of a cork of a preferred embodiment of the invention. The axially facing end surface of the cork includes an annular outer region (7) that encloses an inner region (8). Whilst the region (8) is shown as approximately circular it could, in theory be any shape. In addition whilst in the embodiment shown there are only two regions there could in theory be any number of regions. The recesses in the outer region are formed by a plurality of grooves which form a generally crosshatch pattern. In the inner region the recesses are indentations which, although shown as regularly spaced in the figure may be randomly placed at any point in the inner region. A number of embodiments may be envisaged that follow this general pattern with the axially facing end surface being divided into a number of regions with each region having a different type of recess.

In figure 12 there is illustrated an embodiment wherein the end (1) has a film (F) which covers the end of the cork. The end includes a series of grooves that form a corrugated pattern as well as a taper (T) at the periphery.

Figures 13A, 13B and 13C depict preferred embodiments of the end of the cork of the invention. Figure 13A depicts a castellated end wherein the recesses in the end are spaced apart by a distance (z) and have a width (w). As before the values of z and w may vary greatly however it is preferred that each is in the range of 0.1 to 10 mm, more preferably 0.05 to 7mm, most preferably 0.1 to 5 mm. Figure 13B depicts another preferred embodiment in which the recesses are grooves with a generally v shaped cross-section leading to a concertina type corrugation. Figure 13C depicts yet another preferred embodiment where there are a series of protrusions on the end in the form of ridges extending across the end of the stopper.

Finally figure 14 depicts in plan view a further preferred embodiment of the invention. As with the stopper of figure 11 the axially facing end surface of the cork shows an annular outer region (7) that encloses an inner region (8). The

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recesses in the outer region (7) are formed by a plurality of grooves ( $R_T$ ) that extend radially inwardly from the periphery of the cork. In the inner region (8) the recesses are concentric grooves ( $R_F$ ).

In some of the embodiments of the invention there is a tapered end also incorporated with the other features mentioned previously. The taper provided at the end of the cork body in the various example of the present invention naturally results in the area of the endmost surface being less than the maximum cross-sectional area of the cylindrical stopper body. It is found that only minor reductions in area at the end of the body are required to provide desirable outcomes. The taper may be such that the area at the endmost surface is less than 98 percent of the maximum cross-sectional area of the body, preferably less than 95 percent, more preferably less than 85 percent, and most preferably between 75 percent and 85 percent of the cross-sectional area of the body. Without wishing to be bound by theory, it is thought that such reduction allows for the control of the compression of the film during compression of the stopper body for insertion into the container.

It has been found that any of a number of different tapers can be used to achieve this desired result. For example, the taper may be a uniform or a non-uniform taper. It is preferred, however, that the taper is a uniform taper as this is the form that is most easily mass-produced, and therefore the most desirable from an economic standpoint. At least in principle, however, any type of taper, even stepwise tapers, may be used. Thus, the taper may be straight or curved in shape. It is preferred, however, that the taper not be so extreme that the area of the stopper body on which the film is located becomes smaller than the opening of the bottle it is intended to seal. If this occurs, there is a compromise of the effectiveness of the seal.

One preferred method of forming the taper of the stopper body is to produce a stopper and then chamfer the end to achieve a tapered stopper body. This chamfer step can occur either before or after the attachment of a film. In addition to machining a stopper body (either before or after application of a film) to achieve the taper discussed above, the taper can also be achieved by

attaching a tapered layer or disc to the end of a preformed stopper to produce a composite stopper body with a tapered region at one end. Whilst this technique can be utilised, it is not preferred as it is not cost-effective as these stoppers then become expensive to produce relative to the machining technique.

With stoppers formed according to the present invention, it is typical that the stopper body will have two ends, and each of the two ends will have the same configuration. The advantage of this is that stoppers can then be used in conventional corking machines, and no discrimination between the two ends of the stoppers is required. Therefore, using stoppers with two ends each having the same shape allows the stoppers to perform their desired function irrespective of the capping technique used.

The present invention also provides an improved method of forming stopers that may be used to from the stoppers of the invention. The method includes the steps of:

- (a) providing a container stopper, said stopper having a body of compressible material having at least one end, said end presenting a surface;
- (b) providing a film,

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- (c) heating the film,
- (d) pressing the film and the surface relatively together so as to attach the film to the surface,
- (e) pressing the product of step (d) with a cooling plate, the cooling plate being shaped in such a manner to introduce protrusions or recesses onto the end of the stopper after cooling, wherein step (c) occurs either prior to or simultaneously with step (d).

Once the stopper has been provided in the desired orientation for application of a film, a film is provided. The films provided in the method step are those previously discussed. In a preferred embodiment, the film is provided as a continuous film, spooled between two film holding elements. As such, the film typically spools between these film holding elements. The film holding elements are preferably arranged so as to be able to cooperate to advance the film in either direction as required. The film holding elements are preferably arranged or

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oriented such that that one surface of the film is in substantially the same plane as the end of the stopper to which the film is intended to be attached. It is preferred that the film comprises an adhesive layer and that the orientation of the film is such that the side of the film opposing the end of the stopper has the adhesive layer as an outer layer of the film.

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There are a number of ways in which the relative pressing together of the film and the stopper can be achieved. Thus, for example, the film can be held in place and the stopper pressed against the film. If this is the case, a backing plate is typically utilised to ensure the film does not deform away from the stopper on pressing. Alternatively, both film and die may move relative to each other to compress the stopper and film together. It is preferred, however, that the stopper is held relatively rigidly and the film pressed onto the end of the stopper by way of a backing plate. It is preferred that the pressing is carried out with sufficient force to compress the compressible body of the stopper by at least 5 percent, preferably by at least 10 percent. The pressing step can, in theory, be carried out for any period. It is preferred, however, that it is carried out for between 0.1 to 60 seconds, more preferably 0.1 to 15 seconds, most preferably 0.1 to 5 seconds.

In the process of the invention the film is heated either prior to or simultaneously with the pressing step (d). The heating may be achieved in a number of ways including pre-heating of the film prior to the pressing step. The heating can also be applied by heating the die or clamp holding the stopper or, alternatively, the backing plate that forces the film on to the stopper, can be at an elevated temperature which is transferred to the film on pressing. It is preferred that the film and the surface are pressed relatively together whilst simultaneously heating the film so as to attach the film to the surface. It is preferred that the heating is such that the film is heated to a temperature to soften, melt or activate the layer closest to the stopper, typically at least 40°C, preferably at least 80°C, more preferably at least 110°C, even more preferably at least 150°C, most preferably 180°C.

The heating step is followed by a cooling step using a shaped plate being pressed onto the film. The surface of the plate contains surface features that

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correspond to the surface protrusions or recesses desired in the final stopper. The plate must be pressed with sufficient force to shape the surface of the stopper. It is preferred that the pressing is carried out with sufficient force to compress the compressible body of the stopper by at least 5 percent, preferably by at least 10 percent. The pressing step can, in theory, be carried out for any period. It is preferred, however, that it is carried out for between 0.1 to 60 seconds, more preferably 0.1 to 15 seconds, most preferably 0.1 to 5 seconds.

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The process of invention can occur in such a way that only one end of the stopper is treated or, alternatively, both ends of the stopper can be simultaneously treated by the process described above. In this manner, two backing plates are utilised with two polymeric films. Upon completion of the pressing step, the backing plate or plates are released so as to reduce pressure and the film advanced, a further stopper being provided and the process repeated. One way of achieving this is to have a number of dies arranged on an axle or slide wherein the axle or slide advances to a further position to present a new stopper to be treated and the treated stopper is punched out and replaced with a new stopper. This allows the process to be relatively efficient and time and cost-effective and can therefore be run as a continuous process.

Finally, it will be appreciated that various alterations and/or additions may be introduced into the particular construction and arrangement of parts specifically described with reference to the drawings without departing from the spirit or ambit of the present invention.